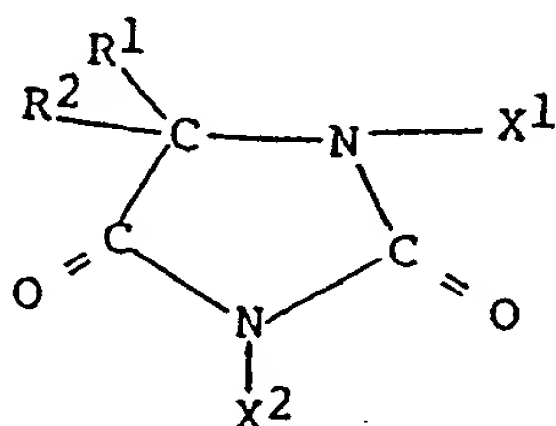


PCT

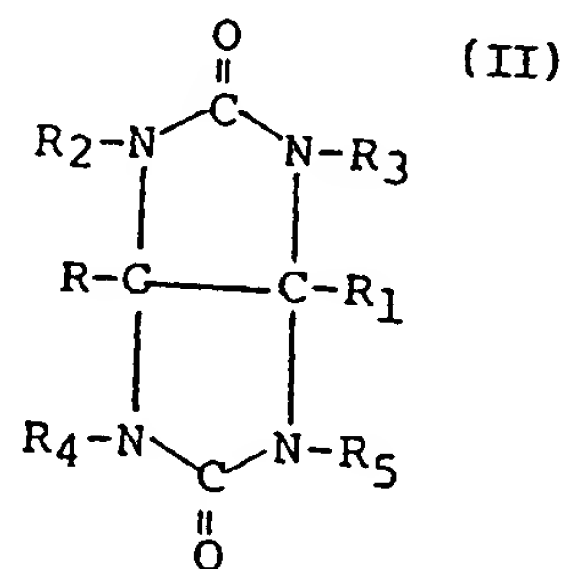
WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : <b>A01N 59/00</b>		<b>A1</b>	(11) International Publication Number: <b>WO 89/10696</b>
		(43) International Publication Date: 16 November 1989 (16.11.89)	
(21) International Application Number: <b>PCT/US89/01700</b> (22) International Filing Date: <b>24 April 1989 (24.04.89)</b> (30) Priority data: 190,395                      5 May 1988 (05.05.88) <b>US</b> (71) Applicant: <b>GREAT LAKES CHEMICAL CORPORATION [US/US]; Post Office Box 2200, West Lafayette, IN 47906 (US).</b> (72) Inventor: <b>PUZIG, Edward, H. ; Post Office Box 2200, West Lafayette, IN 47906 (US).</b> (74) Agents: <b>HEJLEK, Edward, J. et al.; Senniger, Powers, Leavitt &amp; Roedel, 611 Olive St., Suite 2050, St. Louis, MO 63101 (US).</b>		(81) Designated States: <b>AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).</b>  <b>Published</b> <i>With international search report.</i>	
(54) Title: <b>BIOCIDAL COMPOSITION</b>			



(I)



(II)

## (57) Abstract

A dry biocidal composition, the active ingredient of which comprises an N-halo organic oxidizing biocide and a non-oxidizing biocide, the N-halo organic oxidizing biocide being selected from the group consisting of 3-chloro-4,4-dimethyl-2-oxazolidinone, 3-bromo-4,4-dimethyl-2-oxazolidinone, 1,3-dichloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3-dibromo-4,4,5,5-tetramethyl-2-imidazolidinone, 1-bromo-3-chloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3,5-trichloro-s-triazine-2,4,6-trione, dichloro-s-triazine-2,4,6-trione, sodium dichloroisocyanurate, potassium dichloroisocyanurate, N-halohydantoin compounds of formula (I), where R<sup>1</sup> and R<sup>2</sup> are independently selected from the group consisting of hydrogen and lower alkyl, and x<sup>1</sup> and x<sup>2</sup> are independently selected from the group consisting of bromine, chlorine and hydrogen, at least one of x<sup>1</sup> and x<sup>2</sup> being halogen, and N-haloglycourils having formula (II), wherein R and R<sub>1</sub> are each selected from the group consisting of hydrogen, lower alkyl and monocarbocyclic aryl; wherein R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are each selected from the group consisting of hydrogen, chlorine and bromine; and wherein at least one of said R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> is chlorine and at least another of said R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> is bromine; and the non-oxidizing biocide being selected from the group consisting of 2-chloro-4,6-bis(ethylamino)-s-triazine, 2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine, 2-chloro-4,6-bis(isopropylamino)-s-triazine, and 2-chloro-4 ethylamino-6-isopropylamino-s-triazine.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MR	Mauritania
BB	Barbados	GA	Gabon	MW	Malawi
BE	Belgium	GB	United Kingdom	NL	Netherlands
BF	Burkina Fasso	HU	Hungary	NO	Norway
BG	Bulgaria	IT	Italy	RO	Romania
BJ	Benin	JP	Japan	SD	Sudan
BR	Brazil	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LI	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

BIOCIDAL COMPOSITIONBackground of the Invention

This invention relates to a novel biocide, and more particularly to a dry biocidal composition containing an oxidizing biocide and a non-oxidizing biocide.

Routine maintenance of water-cooling towers, swimming pools, hot tubs, and other water systems requires that the water be treated to control the growth of algae, bacteria and fungi. However, no one composition is highly effective against the commonly encountered strains of these pests. For instance, certain compositions are highly effective against the commonly encountered strains of algae, but tend to be less effective against the commonly encountered strains of bacteria or fungi. Other compositions tend to be highly effective against the commonly encountered strains of bacteria, but less effective against the commonly encountered strains of algae or fungi.

Effective use of a single composition in water treatment, therefore, requires the use of a concentration that is great enough to demonstrate activity against the commonly encountered strains of all three pests. However, the use of relatively high concentrations of one component may create problems with the surrounding environment. For instance, it is reported in U.S. patent 4,659,359 that in order to control algae, simazine must be used at a concentration which renders it harmful to plants of a higher order. Also, the cost of maintaining the composition at that concentration may be prohibitive.

An alternative approach that has been tried is the use of two biocides in combination. However, many biocides are not stable to active halogen. For example, in U.S. patent 4,659,359 it is reported that certain triazines

(i.e., ametryne, prometryne and terbutryne) are effective in controlling algae in natural lakes, but cannot be used in chlorinated water tanks, since the compounds are not stable to chlorine. Nevertheless, that patent does suggest that 2-chloro-4,6-bis-(ethylamino)-s-triazine (simazine) and 2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine (terbuthylazine) are stable to chlorine under use conditions in an aqueous state, i.e., at concentrations of 0.1 to 1 mg./l triazine and 0.05 to 3 mg./l active chlorine (col. 3, lines 17-21) and discloses separate treatment of a water system with a source of chlorine and the specified triazines.

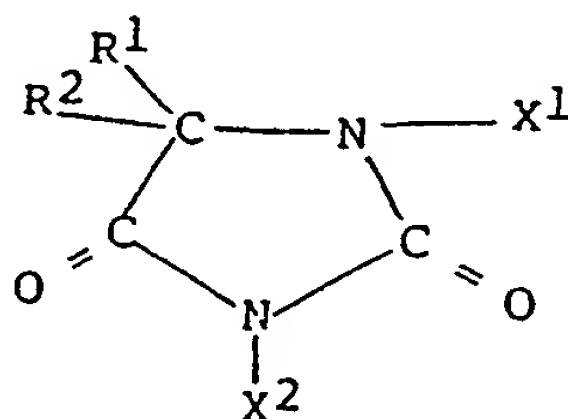
Although separate treatment of water systems with two biocidal compositions may be effective in controlling algae and bacteria, it can be labor intensive. The person responsible for water treatment must separately measure the correct amount of each composition, add it to the system at the appropriate interval and keep records for each. In contrast, continuous feed by means of erosion feeders and the like offers significant labor savings, but is not particularly well suited for treatment of a water system with separate compositions. Either separate feeders for each composition is required or both compositions must be added to the same feed tank. Both options present disadvantages. Separate feeders adds additional expense and requires maintenance of two pieces of equipment instead of one. And because many compositions are not stable to each other at high concentrations, it often is not possible to add both compositions to the same feed tank.

### 30 Summary of the Invention

Among the several objects of the present invention, therefore, may be noted the provision of a biocidal product that is effective for the treatment of

water systems for algae, bacteria and fungi, and which is well suited for use in erosion feeders and for batch-wise addition to a water system. Another object of this invention is the provision of such composition in a "user-friendly" form, wherein the composition is in the form of a solid agglomerate, such as a tablet, which provides an effective amount of each biocidal component and which is stable in the dry state as well as in the effluent of an erosion feeder.

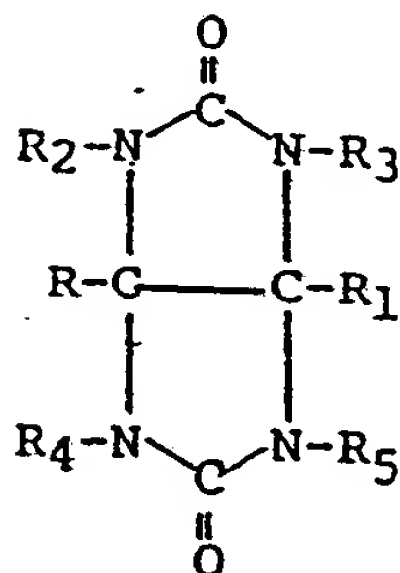
Briefly, therefore, the present invention is directed to a novel dry biocidal composition, the active ingredient of which comprises an oxidizing biocide and a non-oxidizing biocide. The oxidizing biocide is an N-halo organic oxidizer selected from the group consisting of 3-chloro-4,4-dimethyl-2-oxazolidinone, 3-bromo-4,4-dimethyl-2-oxazolidinone, 1,3-dichloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3-dibromo-4,4,5,5-tetramethyl-2-imidazolidinone, 1-bromo-3-chloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3,5-trichloro-s-triazine-2,4,6-trione, dichloro-s-triazine-2,4,6-trione, sodium dichloroisocyanurate, potassium dichloroisocyanurate, N-halohydantoin compounds of the formula



where  $R^1$  and  $R^2$  are independently selected from the group consisting of hydrogen and lower alkyl, and  $X^1$  and  $X^2$  are independently selected from the group consisting

4

of bromine, chlorine and hydrogen, at least one of  $x^1$  and  $x^2$  being halogen and N-haloglycourils having the formula



wherein R and  $R_1$ , are each selected from the group  
 5 consisting of hydrogen, lower alkyl and monocarbocyclic  
 aryl; wherein  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  are each selected  
 from the group consisting of hydrogen, chlorine and  
 bromine; and wherein at least one of said  $R_2$ ,  $R_3$ ,  $R_4$   
 and  $R_5$  is chlorine and at least another of said  $R_2$ ,  
 10  $R_3$ ,  $R_4$  and  $R_5$  is bromine. The non-oxidizing biocide  
 is selected from the group consisting of 2-chloro-  
 4,6-bis(ethylamino)-s-triazine (simazine), 2-(tert-  
 butylamino)-4-chloro-6-(ethylamino)-s-triazine  
 (terbuthylazine), 2-chloro-4,6-bis-(isopropylamino)-  
 15 s-triazine (propazine), and 2-chloro-4 ethyl-amino-  
 6-isopropylamino-s-triazine (atrazine).

The invention is further directed to a solid  
 agglomerate comprising the biocidal composition of this  
 invention. Upon dissolution in water, the agglomerate  
 20 provides an effective amount of active halogen and triazine  
 (simazine, terbuthylazine, atrazine, propazine or a  
 combination thereof). The tablets may optionally include  
 one or more inert ingredient selected from among binders,  
 hardening agents, die lubricants, stabilizers and corrosion  
 25 inhibitors.

The invention is further directed to a method of controlling the growth of algae and bacteria in a water system. The method comprises treating the water system with an effective amount of the biocidal composition of this invention.

Other objects and features of this invention will be in part apparent and in part pointed out hereinafter.

#### Brief Description of the Drawings

FIG. 1 is a graph showing the water temperature on the upper deck and in the basin of the cooling tower versus time as described in Example 3.

FIG. 2 is a graph showing the weight of the biofilm on a portion of the upper deck of the cooling tower and the concentration of algacide in the cooling water versus time as described in Example 3.

FIG. 3 is a graph showing the weight of the biofilm on a portion of the upper deck of the cooling tower and the concentration of algacide in the cooling water versus time as described in Example 3.

#### Description of a Preferred Embodiment

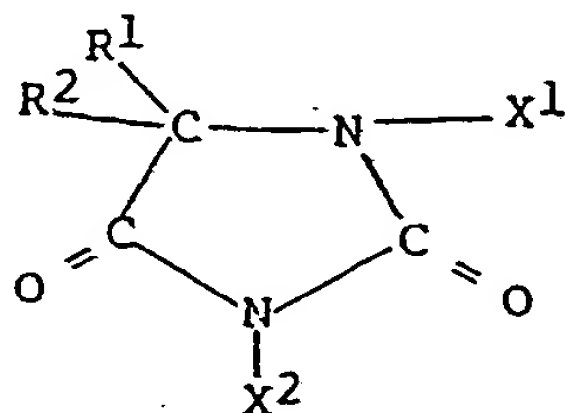
In accordance with this invention, a biocidal product has been discovered which comprises an oxidizing biocide and a non-oxidizing biocide. The product thus provides effective control of bacteria and algae, at concentrations of each component that are less than that required if either component were used alone. Significantly, it has been found that the dry product is stable, i.e., it does not undesirably react when blended in a dry form as measured by the absence of the liberation of halogen gas for a 120 day period at a temperature of 120°F. Moreover, it has surprisingly been found that the oxidizing and non-oxidizing biocides are stable in the

6

aqueous phase, even in the effluent of erosion feeders where the concentrations of each biocidal composition are considerably greater than their respective normal use concentrations in the water system.

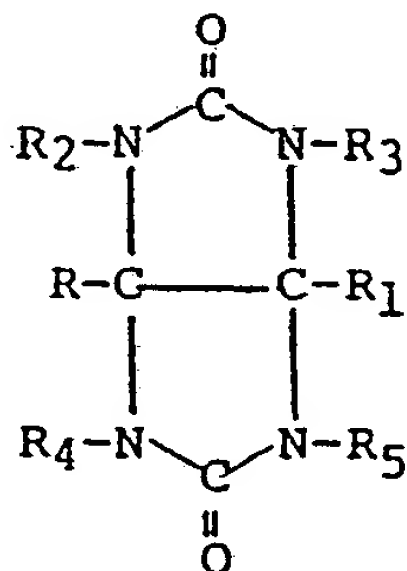
- 5           Oxidizing biocides having application in the present invention include 3-chloro-4,4-dimethyl-2-oxazolidinone, 3-bromo- 4,4-dimethyl-2-oxazolidinone, 1,3-dichloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3-dibromo-4,4,5,5-tetramethyl-2-imidazolidinone, 1-bromo-  
10 3-chloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3,5-trichloro-s-triazine-2,4,6-trione, dichloro-s-triazine-2,4,6-trione, sodium dichloroisocyanurate, potassium dichloroisocyanurate, N-halohydantoin compounds of the formula

15



- where  $R^1$  and  $R^2$  are independently selected from the group consisting of hydrogen and lower alkyl, and  $X^1$  and  $X^2$  are independently selected from the group consisting of bromine, chlorine and hydrogen, at least one of  $X^1$  and  $X^2$  being halogen and N-haloglycourils having the formula:

20





wherein R and R<sub>1</sub>, are each selected from the group consisting of hydrogen, lower alkyl and monocarbocyclic aryl; wherein R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are each selected from the group consisting of hydrogen, chlorine and bromine; and wherein at least one of said R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> is chlorine and at least another of said R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> is bromine. The above-identified N-halohydantoins, in general, and the N,N'-dihalo-hydantoin compounds such as 1-bromo-3-chloro-5,5-dimethylhydantoin, 3-bromo-1-chloro-5,5-dimethylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin, in particular, are preferred as the halogen donor. The most preferred halogen donor is 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH).

Non-oxidizing biocides having application in the present invention include simazine, terbuthylazine propazine and atrazine and mixtures thereof. Commercially available sources of simazine and terbuthylazine presently include a dry herbicide containing 90% simazine and 10% inert ingredients sold under the trade designation Princep Caliber 90 by Ceiba-Geigy (Greensboro, N.C.); and a dry herbicide containing 96% terbuthylazine and 4% inert ingredients sold under the trade designation Bellacide 320 by Ceiby-Geigy.

Preferably, the biocidal product comprises about 1% to about 50% by weight triazine and about 1% to 50% by weight N-halo organic oxidizer, based on the weight of the biologically active ingredient, i.e., N-halo organic oxidizer and non-oxidizing biocide. More preferably, the biocidal composition comprises about 1% to about 25% by weight triazine and about 75% to 99% by weight N-halo organic oxidizer, and most preferably, the biocidal composition comprises about 10% to about 20% by weight triazine and about 80% to 90% by weight N-halo organic

oxidizer, based on the weight of the biologically active ingredient.

As demonstrated in the below examples, a product containing a blend of one of the above-identified active halogen donors and one or more of the above-identified triazines demonstrates no antagonistic effects upon the efficacy of each individual component. It has additionally been discovered that simazine, terbutylazine, atrazine and propazine are stable to active halogen, even at relatively high levels of active halogen. Thus, the dry composition of this invention is particularly well suited for tableting (or the formation of other solid agglomerates) and use in erosion feeders, where the concentration of free halogen in the erosion tank is regularly between about 25 to about 500 ppm, and on occasions will exceed 500 ppm.

Depending upon the water system being treated, and whether it is desired to "shock" the system versus routine maintenance of it, the biocidal product may be in the form of granules, tablets or other solid agglomerates. Particularly where it is desired to "shock" the system, a granulated product is preferred. Granules are conveniently prepared by blending powders of the oxidizing biocide and triazine(s), roller compacting the blend, crushing the compacted material and sieving the crushed material. Preferably, the granules have a sieve size of greater than 90% -10 mesh and greater than 95% +60 mesh. Co-compaction is particularly preferred because it results in a thorough and intimate mixing of the oxidizing biocide and triazine. The granular product may also include inert ingredients that enhance the dissolution of the granules, such as sodium chloride, borax and sodium carbonate.

Particularly where erosion feeders are used, it is preferred that the biocidal product be in the form of a tablet (or other solid agglomerate). Through the use of

stabilizers, binders, dissolution agents and hardening agents, the tablet can be designed to disintegrate at a particular rate, thus delivering the active biocidal ingredients to the system in a controlled, time-release manner. Preferred hardening agents for the tablets include dry particulate alkali metal or alkaline earth salts consisting of a cation selected from among the group comprising lithium, sodium, potassium, calcium, and magnesium and an anion selected from among the group comprising carbonate, bicarbonate, borate, silicate, phosphate, percarbonate, and perphosphate. The preferred binders are methyl cellulose, sodium-carboxy-methyl cellulose, polyvinyl alcohol, sodium alginate, gums, resins, zeolites, sodium silicate, starch, stearic acid, metallic stearates, glycols, carbowax and water. The preferred dissolution agents are sodium chloride, borax and sodium carbonate.

Tablets are formed by blending dry particulate halogen donor and dry particulate triazine with additive (in a dry, particulate form) to form a mixture and transferring the mixture to a tableting machine such as a Stokes rotary press. Preferably, a die lubricant such as sodium stearate is included in the tableted composition. Conventional blending equipment is used, a twin shell or Vee mixer being particularly preferred. The amount of additive blended with the halogen donor and triazine is determined by the concentrations desired in the final product. Through the use of additives mentioned above, the tablets may be designed for either fast dissolution (shocking applications) or slow dissolution in an erosion tank.

The resulting tablets may vary in size depending upon the application. However, it has been found that

tablets of about 1 3/16" diameter and of about 3" in diameter (sometimes referred to as "pucks") are preferred.

The density of the tablet has an effect upon its dissolution. In erosion tanks, the dissolution of low density tablets is difficult to control. Although it is less difficult to control the dissolution of higher density tablets, if the density gets too high, the dissolution rate decreases to such an extent that a larger capacity erosion tank is required. Therefore, it is preferred that the tablets have a density between about 1.2 and about 1.7 gm./cc.

The biocidal composition of this invention may additionally include halogen stabilizers, such as dimethylhydantoin or cyanuric acid; ultraviolet light stabilizers such as cyanuric acid, dimethylhydantoin, and oxazolidinone; and corrosion inhibitors such as sodium zinc polyphosphate ( $\text{Na}_{1/2n+1} \text{Zn}_{1/2n+1} \text{P}_n \text{O}_{3n+1}$ ) and sodium hexametaphosphate ( $\text{Na}_{n+2} \text{P}_n \text{O}_{3n+1}$ ) where  $n = 10-16$ . The amount of corrosion inhibitor and stabilizers, will of course, be determined by the application for the product. In general, however, it is preferred that the biocidal composition contain between about 5 to 50% by weight of the halogen stabilizer, between about 5 to 50% by weight of the ultraviolet light stabilizer, and between about 5 to 50% by weight of the corrosion inhibitor, based on the weight of the biocidal product (including additives).

Where the biocide product of this invention is prepared by using one of the above-identified commercially available sources of simazine or terbuthylazine, such as Princep Caliber 90, it is particularly preferred that the product contain a halogen stabilizer. The inert ingredients of Princep Caliber 90 include clays and surfactants which may cause decomposition of the N-halo organic oxidizers in the absence of halogen stabilizers.

11

Although the concentration will vary depending upon the water system, it is generally preferred that the concentration of halogen and the concentration of triazine (simazine, terbuthylazine, atrazine, propazine or a combination thereof) in the water system be maintained at a level between about 0.1 to about 50 parts per million (ppm) of halogen (measured as chlorine) and between about 0.1 to about 10 ppm triazine to keep the system free of algae, bacteria and fungi. For many water systems such as water cooling towers and swimming pools, it is particularly preferred that the concentration of halogen and triazine be maintained at about 1-3 ppm and 1 ppm, respectively. Thus, in a preferred embodiment of the present invention, the relative amounts of N-halo organic oxidizer and triazine in the biocidal product are tailored so that upon regular (or continuous) treatment of the water system, the preferred levels of active halogen and triazine are maintained, taking into account loss from the system through blow down, dilution or other causes.

As used herein, parts per million of halogen refers to the level of free halogen and not total halogen, except where indicated. The number of parts per million of active halogen is determined as per AWWA chlorine method and the number of parts per million of triazine is determined by HPLC.

In a particularly preferred embodiment, the biocidal product is in the form of a solid, shaped agglomerate such as a tablet. Preferably, the tablets not only provide the desired ratio of halogen and triazine (e.g., 1-3 parts halogen: 1 part triazine) but are designed to do so in a predetermined volume of water. For instance, because most spas contain a relatively small volume of water, it is preferable to use a tablet that provides 3 ppm of halogen and 1 ppm triazine per 250 gallons or 500

gallons of water. In contrast, for swimming pools and large capacity cooling towers, it is preferable to use a tablet that provides 3 ppm of halogen and 1 ppm of triazine per 1,000 or 10,000 gallons of water. The provision of the biocidal product in tablets that provide the desired concentrations of halogen and triazine upon dissolution in a predetermined volume of water allows for relatively simple maintenance of the water system. The operator simply adds the correct number of tablets (i.e., an effective amount) at appropriate intervals to control the growth of algae, bacteria and fungi.

Such tablets are particularly well suited for use in erosion feeders currently being used, for example, in connection with the treatment of swimming pools and cooling towers. Erosion tanks installed on a by-pass line taken from the main pumping line of the water system are filled with the biocidal composition in the form of granules or tablets. A small quantity of the system water from the main pumping line is diverted to the erosion tank where the biocidal composition is dissolved into the water, and the effluent from the erosion tank is returned to the water system. The concentration of biocide in the effluent is dependant upon bed volume of solid biocide, temperature, water flow rate and density of the tablets. Preferably, the concentration of halogen in the effluent is about 10 to 500 ppm of halogen measured as chlorine and the concentration of triazine in the effluent is about 10 to 100 ppm.

Thus, where an erosion tank is employed, the operator need only periodically refill the tank with the biocidal composition in the form of granules or tablets. And because the biocidal composition of the present invention contains both an oxidizing and a non-oxidizing biocide, the operator need do nothing more than

periodically refill the erosion tank with granules or tablets having the desired relative amounts of non-oxidizing and oxidizing biocides to effectively control bacteria, algae and fungi. No additional equipment is necessary, nor is there any need to separately add or keep records regarding any additional biocidal composition.

As mentioned above, it was surprising to find that the N-halo organic oxidizing biocide is stable to both simazine and terbuthylazine when the product is in the form of granules or tablets produced from co-compacted powders of the N-halo organic oxidizing biocide and simazine or terbuthylazine. It was even more surprising that these compositions are stable to each other in erosion tanks where the concentration of halogen ranges from about 25 to 500 ppm and the concentration of triazine ranges from about 2.5 to 50 ppm. Moreover, without being bound to any theory, it is presently believed that in the presence of active halogen, simazine and terbuthylazine are converted to N-halo derivatives which demonstrate greater efficacy as a biocide than does either simazine or terbuthylazine. And the greater the concentration of halogen and triazine in the erosion tank, the greater will be the rate of conversion of simazine and terbuthylazine to the N-halo derivative, i.e., 2-chloro-4,6-bis-(chloro-ethylamino)-s-triazine and 2-(tert-chloro-butylamino)-4-chloro-6-(chloro-ethylamino)-s-triazine.

The following examples illustrate the invention.



14

Example 1

Tablets (20 gm) having the formulations listed below were prepared by cocompacting equimolar quantities of BCDMH, DMH and or cyanuric acid dry blending the granulated formulation ingredients and tableting on a stokes tableting press to the desired weight. The tablets were stored for a 120 day period at a temperature of 120°F and monitored throughout this period for the formation of free bromine. No free bromine was detected. Also, at the conclusion of the 120 day period, each composition was analyzed for bromine content and it was found that each composition contained at least 95 wt. % of the bromine originally contained by the composition.

CN 1171

15 53 wt. % CN 363<sup>a</sup>  
 20 wt. % PC 90<sup>b</sup>  
 24 wt. % Sodium chloride  
 3 wt. % Sodium carbonate

CN 1210

79 wt. % CN 363<sup>a</sup>  
 10 wt. % PC 90<sup>b</sup>  
 8 wt. % Sodium chloride  
 3 wt. % Sodium carbonate

CN 538

20 27.53 wt. % BCDMH  
 7.57 wt. % PC 90<sup>b</sup>  
 27.04 wt. % Sodium Chloride  
 37.86 wt. % Sodium Zinc  
                     Polyphosphate

CN 1168

53 wt. % CN 363<sup>a</sup>  
 10 wt. % PC 90<sup>b</sup>  
 10 wt. % Bellacide 320<sup>c</sup>  
 24 wt. % Sodium chloride  
 3 wt. % Sodium carbonate

25 CN 498

93 wt. % CN 363<sup>a</sup>  
 4 wt. % Aquazine<sup>d</sup>  
 3 wt. % Sodium Metasilicate·5H<sub>2</sub>O



15

CN 49990 wt. % CN 501<sup>e</sup>7 wt. % Aquazine<sup>d</sup>3 wt. % Sodium Metasilicate·5 H<sub>2</sub>O

5   <sup>a</sup>CN 363 is a co-compacted powder comprising 65 wt. % BCDMH and 35 wt.% DMH.

<sup>b</sup>PC 90 is a herbicide sold by Ceiby-Geigy (Greensboro, N.C.) under the trademark Princep Caliber 90 that contains 90% simazine and 10% inert ingredients.

10   <sup>c</sup>Bellacide 320 is a powder sold by Ceiby-Geigy containing 96% terbuthylazine and 4% inert ingredients.

<sup>d</sup>Aquazine is an algacide sold by Ceiby-Geigy (Greensboro, N.C.) containing 80% simazine and 20% inert ingredients.

<sup>e</sup>CN 501 is a co-compacted powder comprising 60 wt.% BCDMH, 15   30 wt.% trichloroisocyanurate and 10 wt % cyanuric acid.

Example 2

## Treatment of a Cooling Tower

     A Marley open double flow cooling tower with 10,000 gallon capacity and 80,000 gallons per day make up  
20   water flow was treated over a 104 day period with a formulation designated CN-530. (The CN-530 used in this example had two separate formulations. The first formulation contained 87% CN-363 (see Example 1), 3% sodium metasilicate pentahydrate and 10% Princep Caliber 90  
25   (PC-90) and the second formulation contained 82% CN-363, 3% sodium metasilicate pentahydrate and 15% PC-90. In the following description, the percent of PC-90 is stated along with the compound number to distinguish the first CN-530 formulation from the second CN-530 formulation).. The tower  
30   used for this test provided a perfect environment for algae

16

growth because the location provided a steady source of nutrients. An erosion-type continuous feed tank, SC-16-10 Brominator with 35 pound tablet discharge capacity, was connected to the make-up water line for the cooling tower and integrated with a H-O-H timed turbine chemical feed controller to measure the CN-530 dosage.

Immediately prior to beginning the test, a portion of the upper deck of the cooling tower was cleaned of algae and another portion was left in an algae-fouled condition. On day 0 and prior to the CN-530 treatment, algae growth was slowed but not controlled, by methylene bithiocyanate, MBT, in conjunction with BromiCide (BCDMH). MBT was applied by slugging at concentrations of 0.25 to 0.75 ppm and BCDMH was fed to maintain a 0.5 to 1.5 ppm free halogen residual measured as bromine by the FACTS technique.

Beginning on day 13, MBT treatment was discontinued and the tower was treated with BromiCide alone. A thin layer, less than 3/8", of algae was then present on the tower distributor. Within one week the algae mat grew one inch.

Beginning on day 20, Bromicide treatment was discontinued and the tower was treated with CN-530 (10% PC-90). The concentration of halogen was maintained at 0.5 to 1.5 ppm measured as bromine and the concentration of simazine was maintained at approximately 2.0 ppm as measured by HPLC. The growth of algae stopped, turned grey, loosened and later became unattached from the tower distributor. However, because the biocide concentration in the cooling water fell below effective levels during the treatment period due to a malfunction of the chemical feed equipment, the algae mat grew back and was mechanically removed on day 48.

After mechanical removal of the algae mat, CN-530 (10% PC-90) treatment was continued at the previous levels. Chemical consumption during the period from day 21 to day 55 averaged 8.8 pounds per day CN-530 (10% PC-90).

5 MBT was slug fed starting on day 57 and concluded on day 66. During this period all remaining algae was killed.

Beginning on day 67, the tower was treated with CN-530 (15% PC-90). However, because of the drop in temperature, less make-up water was required, resulting in  
10 a drop in the dosage of CN-530. As a result, the concentration of algicide in the cooling water dropped to less than 1 part per million and the biofilm weight increased significantly. The test was discontinued on day 104 when the water temperature fell below that which would  
15 promote the growth of algae.

The following will summarize the sampling and analytical methods used.

#### 1. Biofilm Sampling

A 10 cm I.D. pyrex glass flared pipe connector  
20 was used to sample the biofilm on the upper deck of the cooling tower. The open-ended glass cylinder was placed directly on the upper deck and the biofilm was removed by scraping. Three different regions were sampled: a previously fouled area, an area that was entirely clean  
25 (macroscopically) on the first day of the test, and an area that was cleaned on the day that CN-530 treatments began. Two to four different areas in each region on the upper deck were scraped and the biofilm specimens were pooled. The specimens were transported to the laboratory on ice and  
30 then stored frozen until quantitative biofilm analyses were performed.

## 2. Gravimetric Analyses of Biofilms

The dry weight and ash-free weight of biofilm samples were determined essentially as described in Standard Methods for the Examination of Water and Wastewater, 15th Ed. (Method 1002H.4). One to five ml aliquots of homogenized biofilm samples were added to pre-weighed crucibles and dried to constant dry weight at 105 C. Samples were then ignited at 550 C for 1 hr in order to determine ash-free weight. About 0.5 ml of distilled water was added to each crucible to rehydrate the residue and then, dried to constant weight at 105 C in order to correct for the water of rehydration. The difference between the dry weight and the corrected ash-free weight was used to calculate the total volatile residue (which is a measure of the organic weight). Each biofilm sample was analyzed in triplicate.

Figure 1 shows the water temperature (°C) on the upper deck and in the basin of the cooling tower. The water temperature ranged from about 26 to about 34°C on the upper deck; the microbial biofilm was consistently exposed to cooler water after about day 50.

Figure 2 shows the biofilm weight (open symbols) and simazine concentration (closed symbols) of the previously fouled area, i.e., that area not cleaned of algae immediately prior to the test. The data show that the biofilm weight increased dramatically when the MBT was discontinued (day 13); that the increase in biofilm weight stopped when CN-530 treatment began (day 20) and that biofilm development was inhibited until about day 37; that biofilm development began again when the concentration of simazine was consistently below about 2 ppm (day 37-48); and that after the biofilm was removed (day 48), it did not

increase dramatically until the simazine concentration was consistently below about 1 ppm.

Figure 3 shows the biofilm weight (open symbols) and simazine concentration (closed symbols) with time for the surface that was cleaned when the test began. The data show that the biofilm did not increase in weight dramatically until after the algacide concentration had been consistently below about 2 ppm (days 37-48); and that biofilm development was inhibited after cleaning the deck (day 48) until the concentration of algacide dropped to below 1 ppm.

### EXAMPLE 3

Two dissolution rate tests were performed to determine how CN-530 (10% PC-90; see Example 2) tablet dissolution behaviour differs from Bromicide tablets (92.5 wt.% BCDMH, 7.5 wt.% inert ingredients sold by Great Lakes Chemical Corp., Lafayette, Indiana) in the industrial water treatment CBB-35 brominator (Hydrotech, Georgia). The tests were run using a 5 gpm flow rate, 80°F water temperature, and 10 lb charge weight. The free and total bromine measurements were performed with the FAS-DPD system.

The residual delivery rate behavior was relatively flat over the four-hour test period for both CN-530 and BCDMH tablets in the brominator. The average free bromine residual was 84.8 ppm for the CN-530 tablets and 33.9 ppm for the BCDMH tablets. The amount of product consumed by mass balance determination was 2.8 lbs for CN-530 and 0.16 lbs for BCDMH tablets. The delivery rates are listed in Table 1.

20

Table I  
Delivery Rate of CN-530 and BCDMH Tablets

		<u>CN - 530</u>		<u>BCDMH</u>	
	<u>Time</u>	<u>Free Br<sub>2</sub></u>	<u>Total Br<sub>2</sub></u>	<u>Free Br<sub>2</sub></u>	<u>Total Br<sub>2</sub></u>
5	15	55.43	117.2	41.00	86.52
	30	73.00	150.5	35.15	71.20
	45	62.64	130.7	31.54	63.09
	60	70.30	151.0	24.78	65.34
	75	91.48	182.5	29.97	59.70
10	90	72.10	150.5	26.59	56.10
	105	66.24	139.7	32.00	63.09
	120	93.73	162.2	43.94	74.35
	135	91.48	162.7	38.75	68.05
	150	86.07	172.6	37.18	67.82
15	165	104.10	178.9	26.59	56.33
	180	78.00	142.9	32.22	61.51
	195	85.62	150.5	41.01	73.23
	210	116.30	210.9	34.25	64.44
	225	97.79	173.5	30.64	56.78
20	240	111.80	187.0	36.05	65.34

21

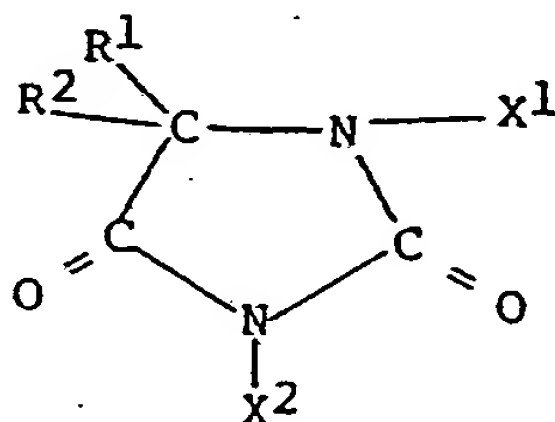
In view of the above, it will be seen that the several objects of the invention are achieved.

As various changes could be made in the above compositions and methods without departing from the scope  
5 of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

## CLAIMS

What is claimed:

1. A dry biocidal composition, the active ingredient of which comprises an N-halo organic oxidizing biocide and a non-oxidizing biocide, the N-halo organic oxidizing biocide being selected from the group consisting of 3-chloro-4,4-dimethyl-2-oxazolidinone, 3-bromo-4,4-dimethyl-2-oxazolidinone, 1,3-dichloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3-dibromo-4,4,5,5-tetramethyl-2-imidazolidinone, 1-bromo-3-chloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3,5-trichloro-s-triazine-2,4,6-trione, dichloro-s-triazine-2,4,6-trione, sodium dichloroisocyanurate, potassium dichloroisocyanurate, N-halohydantoin compounds of the formula

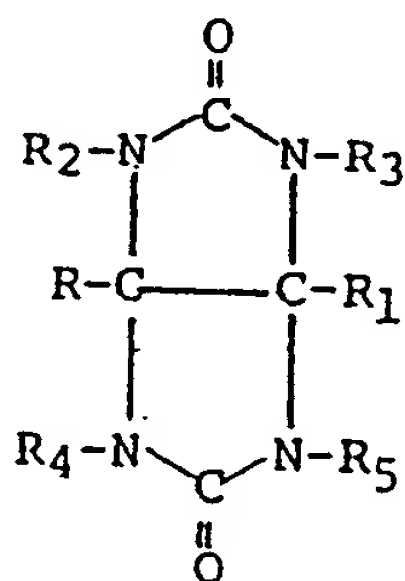




23

15 where  $R^1$  and  $R^2$  are independently selected from the group consisting of hydrogen and lower alkyl, and  $x^1$  and  $x^2$  are independently selected from the group consisting of bromine, chlorine and hydrogen, at least one of  $x^1$  and  $x^2$  being halogen, and N-haloglycourils having the formula:

20



where R and  $R_1$  are each selected from the group consisting of hydrogen, lower alkyl and monocarbocyclic aryl; wherein  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  are each selected from the group consisting of hydrogen, chlorine and bromine; and wherein at least one of said  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  is chlorine and at least another of said  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  is bromine; and the non-oxidizing biocide being selected from the group consisting of 2-chloro-4,6-bis(ethylamino)-s-triazine, 2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine, 2-chloro-4,6-bis(isopropylamino)-s-triazine, and 2-chloro-4-ethyl-amino-6-isopropylamino-s-triazine.

24

2. The biocidal composition of claim 1 wherein said N-halo organic oxidizing biocide is selected from the group consisting of 1-bromo-3-chloro-5,5-dimethylhydantoin, 3-bromo-1-chloro-5,5-dimethylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, and 1,3-dichloro-5,5-dimethylhydantoin.

3. The biocidal composition of claim 1 wherein said N-halo organic oxidizing biocide is 1-bromo-3-chloro-5,5-dimethylhydantoin.

4. The biocidal composition of claim 1 wherein said biocidal composition comprises between about 1% and about 50% by weight of said non-oxidizing biocide and between about 50% and about 99% by weight of said N-halo organic oxidizing biocide, based on the weight of the active ingredient.

5. The biocidal composition of claim 1 wherein said active ingredient comprises between about 1% and about 25% by weight of said non-oxidizing biocide and between about 75% and about 99% by weight of said N-halo organic oxidizing biocide, based on the weight of the active ingredient.

25

6. The biocidal composition of claim 1 wherein said active ingredient consists essentially of between about 10% and about 20% by weight of said non-oxidizing biocide and between about 80% and about 90% by weight of said N-halo organic oxidizing biocide, based on the weight of the active ingredient.

7. A biocidal composition as set forth in claim 1, wherein said composition further comprises between about 5% and about 50% by weight of a halogen stabilizer, based on the weight of the biocidal composition.

8. A biocidal composition as set forth in claim 7, wherein said halogen stabilizer is selected from the group consisting of dimethylhydantoin and cyanuric acid.

9. A biocidal composition as set forth in claim 1 wherein said composition further comprises between about 5% and about 50% by weight of a hardening agent based on the weight of the biocidal composition.

10. A biocidal composition as set forth in claim 9 wherein said hardening agent is an alkali metal or alkaline metal salt consisting of a cation selected from the group consisting of lithium, sodium, potassium, calcium

26

5 and magnesium and an anion selected from the group consisting of carbonate, bicarbonate, borate, silicate, phosphate, percarbonate and perphosphate.

11. A biocidal composition as set forth in claim 1, wherein said composition further comprises between about 5% and about 50% by weight of a dissolution agent, based on the weight of the biocidal composition.

12. A biocidal composition as set forth in claim 11, wherein said dissolution agent is selected from the group consisting of sodium chloride, borax and sodium carbonate.

13. A biocidal composition as set forth in claim 1, wherein said composition further comprises a binder selected from the group consisting of methyl cellulose, sodium-carboxy-methyl cellulose, polyvinyl alcohol, sodium alginate, gums, resins, zeolites, sodium silicate, starch, stearic acid, metallic stearates, glycols, carbowax and water.

14. A biocidal composition as set forth in claim 1, wherein said composition further comprises between

27

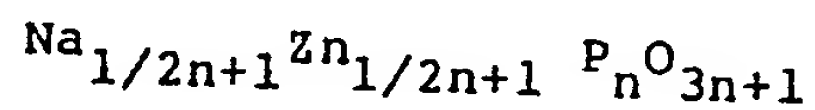
about 5% and about 50% by weight of an ultraviolet light stabilizer, based on the weight of the biocidal composition.

15. A biocidal composition as set forth in claim 14, wherein said ultraviolet light stabilizer is selected from the group consisting of dimethylhydantoin, cyanuric acid and oxazolidinone.

16. A biocidal composition as set forth in claim 1, wherein said composition further comprises between about 5% and about 50% by weight of a corrosion inhibitor, based on the weight of the biocidal composition.

17. A biocidal composition as set forth in claim 16, wherein said corrosion inhibitor is selected from the group consisting of sodium zinc polyphosphates of the formula

5



and sodium hexametaphosphates of the formula

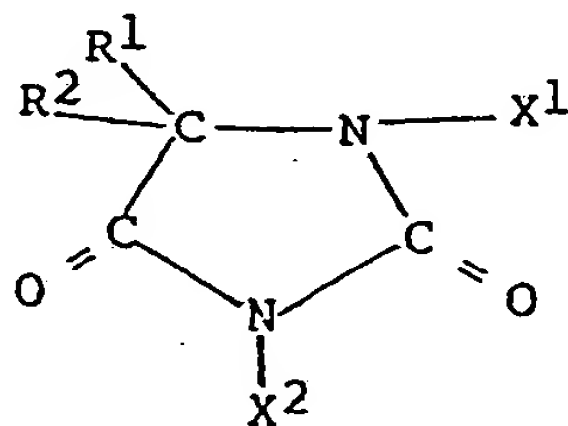


where n is an integer from 10 to 16.

28

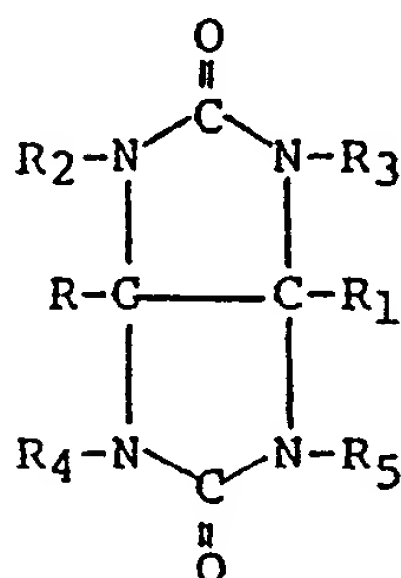
18. A biocidal composition as set forth in claim 1, wherein said composition is granulated.

19. A solid agglomerate for use in controlling the growth of algae and bacteria in a water system, the agglomerate having a density between about 1.2 and about 1.7 gm/cc and comprising an inert ingredient selected from the group consisting of binders, hardening agents, dissolution agents and stabilizers and a bioactive ingredient comprising an N-halo organic oxidizer and a non-oxidizing biocide, the N-halo organic oxidizer being selected from the group consisting of 3-chloro-4,4-dimethyl-2-oxazolidinone, 3-bromo-4,4-dimethyl-2-oxazolidinone, 1,3-dichloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3-dibromo-4,4,5,5-tetramethyl-2-imidazolidinone, 1-bromo-3-chloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3,5-trichloro-s-triazine-2,4,6-trione, dichloro-s-triazine-2,4,6-trione, sodium dichloroisocyanurate, potassium dichloroisocyanurate, N-halohydantoin compounds of the formula



29

where  $R^1$  and  $R^2$  are independently selected from the group consisting of hydrogen and lower alkyl, and  $x^1$  and  $x^2$  are independently selected from the group consisting of bromine, chlorine and hydrogen, at least one of  $x^1$  and  $x^2$  being halogen, and N-haloglycourils having the formula:



where  $R$  and  $R_1$ , are each selected from the group consisting of hydrogen, lower alkyl and monocarbocyclic aryl; wherein  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  are each selected from the group consisting of hydrogen, chlorine and bromine; and wherein at least one of said  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  is chlorine and at least another of said  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  is bromine; and the non-oxidizing biocide being selected from the group consisting of

2-chloro-4,6-bis(ethylamino)-s-triazine,  
 2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine  
 2-chloro-4,6-bis-(isopropylamino)-s-triazine, and  
 2-chloro-4 ethylamino-6-isopropylamino-s-triazine.

20. The biocidal composition of claim 19 wherein said N-halo organic oxidizing biocide is selected from the group consisting of 1-bromo-3-chloro-5,5-dimethylhydantoin, 3-bromo-1-chloro-5,5-dimethylhydantoin, 5 1,3-dibromo-5,5-dimethylhydantoin, and 1,3-dichloro-5,5-dimethylhydantoin.

21. An agglomerate as set forth in claim 19, wherein said N-halo organic oxidizing biocide is 1-bromo-3-chloro-5,5-dimethylhydantoin.

22. An agglomerate as set forth in claim 19, wherein said agglomerate upon dissolution provides active halogen and non-oxidizing biocide in the ratio of about 1 to 3 parts active halogen measured as chlorine to 1 part 5 non-oxidizing biocide.

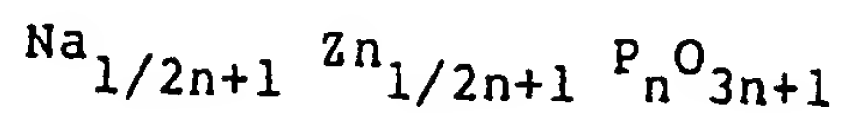
23. An agglomerate as set forth in claim 19, wherein said agglomerate comprises between about 5 and about 50% by weight of a corrosion inhibitor, based on the weight of the agglomerate.

24. An agglomerate as set forth in claim 23, wherein said corrosion inhibitor is selected from the group



31

consisting of sodium zinc polyphosphates of the formula



5 and sodium hexametaphosphates of the formula



where n is an integer from 10 to 16.

25. An agglomerate as set forth in claim 19, wherein said agglomerate comprises between about 5 and 50% by weight of an ultraviolet light stabilizer, based on the weight of the agglomerate.

26. An agglomerate as set forth in claim 25, wherein said ultraviolet light stabilizer is selected from the group consisting of dimethylhydantoin, cyanuric acid and oxazolidinone.

27. An agglomerate as set forth in claim 19, wherein said agglomerate comprises between about 5 and 50% by weight of a halogen stabilizer, based on the weight of the agglomerate.

28. An agglomerate as set forth in claim 27, wherein said halogen stabilizer is selected from the group consisting of dimethylhydantoin, and cyanuric acid.

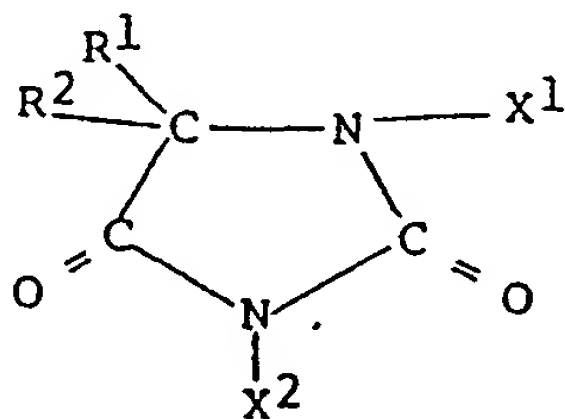
29. An agglomerate as set forth in claim 19 wherein said bioactive ingredient comprises between about 1% and about 99% by weight of said non-oxidizing biocide and between about 1% and about 99% by weight of said N-halo organic oxidizing biocide, based on the weight of the bioactive ingredient.

30. An agglomerate as set forth in claim 19 wherein said bioactive ingredient comprises between about 1% and about 25% by weight of said non-oxidizing biocide and between about 75% and about 99% by weight of said N-halo organic oxidizing biocide, based on the weight of the bioactive ingredient.

31. An agglomerate as set forth in claim 19 wherein said bioactive ingredient consists essentially of between about 10% and about 20% by weight of said non-oxidizing biocide and between about 80% and about 90% by weight of said N-halo organic oxidizing biocide, based on the weight of the active ingredient.

33

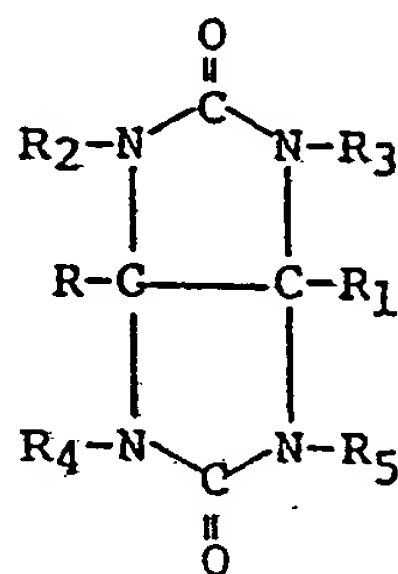
32. A method of controlling the growth of algae and bacteria in a water system comprising treating the water system with an effective amount of a dry biocidal composition containing an N-halo organic oxidizing biocide and a non-oxidizing biocide as the bioactive ingredient, the N-halo organic oxidizing biocide being selected from the group consisting of 3-chloro-4,4-dimethyl-2-oxazolidinone, 3-bromo-4,4-dimethyl-2-oxazolidinone, 1,3-dichloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3-dibromo-4,4,5,5-tetramethyl-2-imidazolidinone, 1-bromo-3-chloro-4,4,5,5-tetramethyl-2-imidazolidinone, 1,3,5-trichloro-s-triazine-2,4,6-trione, dichloro-s-triazine-2,4,6-trione, sodium dichloroisocyanurate, potassium dichloroisocyanurate, N-halohydantoin compounds of the formula



where  $R^1$  and  $R^2$  are independently selected from the group consisting of hydrogen and lower alkyl, and  $X^1$  and

34

$x^2$  are independently selected from the group consisting of bromine, chlorine and hydrogen, at least one of  $x^1$  and  $x^2$  being halogen, and N-haloglycourils having the formula:



where R and  $R_1$  are each selected from the group consisting of hydrogen, lower alkyl and monocarbocyclic aryl; wherein  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  are each selected from the group consisting of hydrogen, chlorine and bromine; and wherein at least one of said  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  is chlorine and at least another of said  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  is bromine; and the non-oxidizing biocide being elected from the group consisting of

2-chloro-4,6-bis(ethylamino)-s-triazine,  
 2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine,  
 2-chloro-4,6-bis(isopropylamino)-s-triazine, and  
 2-chloro-4-ethylamino-6-isopropylamino-s-triazine.

35

33. A method as set forth in claim 32, wherein said biocidal composition comprises between about 1% and about 50% by weight of said non-oxidizing biocide and between about 50% and about 99% by weight of said N-halo  
5 organic oxidizing biocide, based on the weight of the bioactive ingredient.

34. A method as set forth in claim 32, wherein said biocidal composition comprises between about 1% and about 25% by weight of said non-oxidizing biocide and between about 75% and about 99% by weight of said N-halo  
5 organic oxidizing biocide, based on the weight of the bioactive ingredient.

35. A method as set forth in claim 32, wherein said biocidal composition is in the form of an agglomerate having density between about 1.2 and about 1.7 gms/cc and which upon dissolution provides active halogen measured as  
5 chlorine and non-oxidizing biocide in the ratio of about 1 to 3 parts halogen to 1 part non-oxidizing biocide.

36. A method as set forth in claim 32 wherein the biocidal composition is contained within an erosion feeder and the water system is treated by passing a stream

36

of water through the erosion feeder and mixing the effluent  
5 from the feeder with the water of the water system.

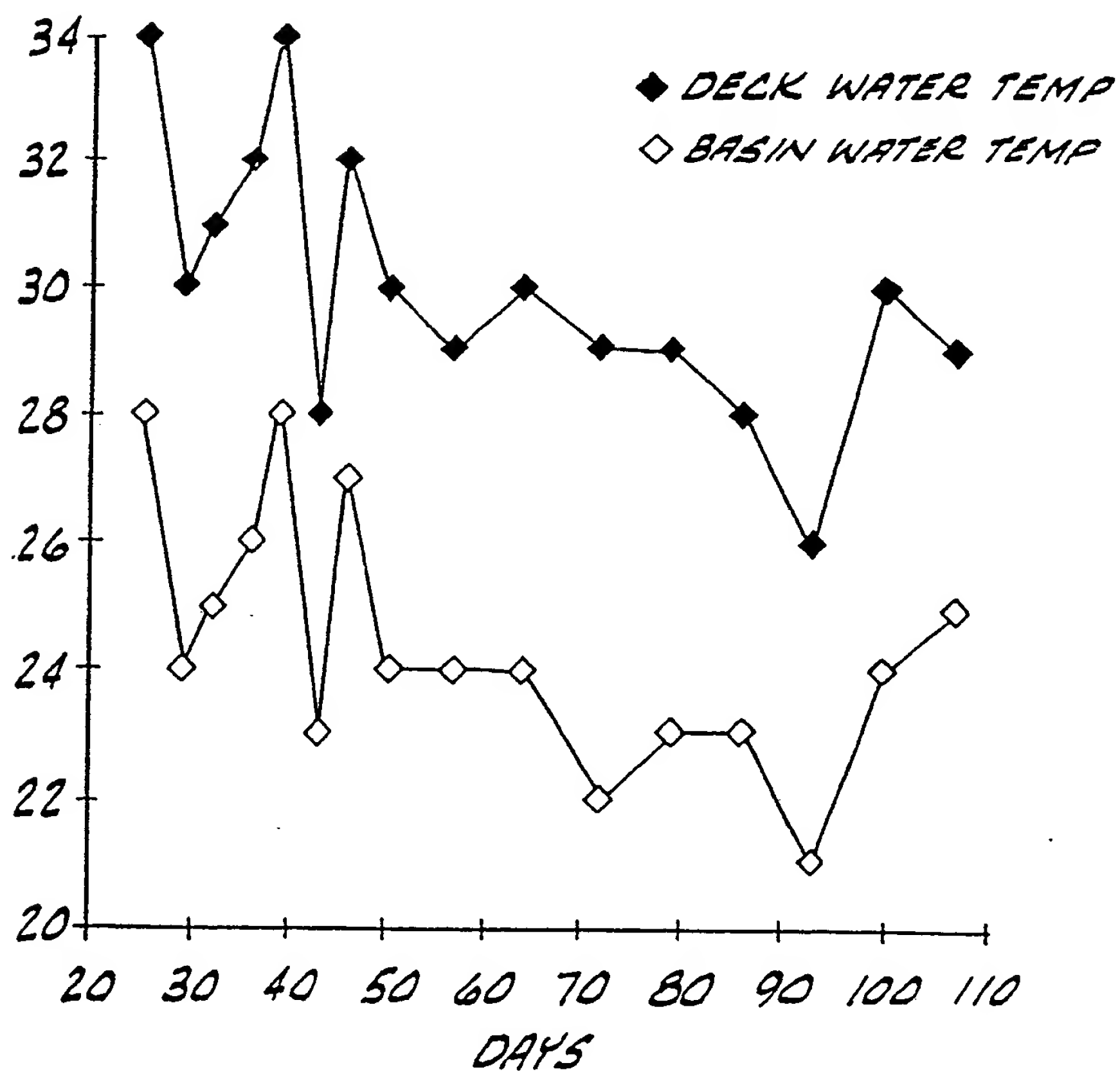
37. A method as set forth in claim 36 wherein  
the concentration of the N-halo organic oxidizing biocide  
and the non-oxidizing biocide in the effluent is between  
about 10 to about 500 ppm and about 10 to about 100,  
5 respectively.

38. A method as set forth in claim 37, wherein  
said non-oxidizing biocide is converted to an N-halo  
derivative in the erosion feeder, the N-halo derivative  
being selected from the group consisting of  
5 2-chloro-4,6-bis-(chloro-ethylamino)-s-triazine and  
2-(tert-chloro-butylamino)-4-chloro-6-(chloro-ethylamino)-s-  
triazine.

1 / 2

FIG.1

WATER TEMPERATURE (°C)  
IN COOLING TOWER SYSTEM



2 / 2

FIG. 2

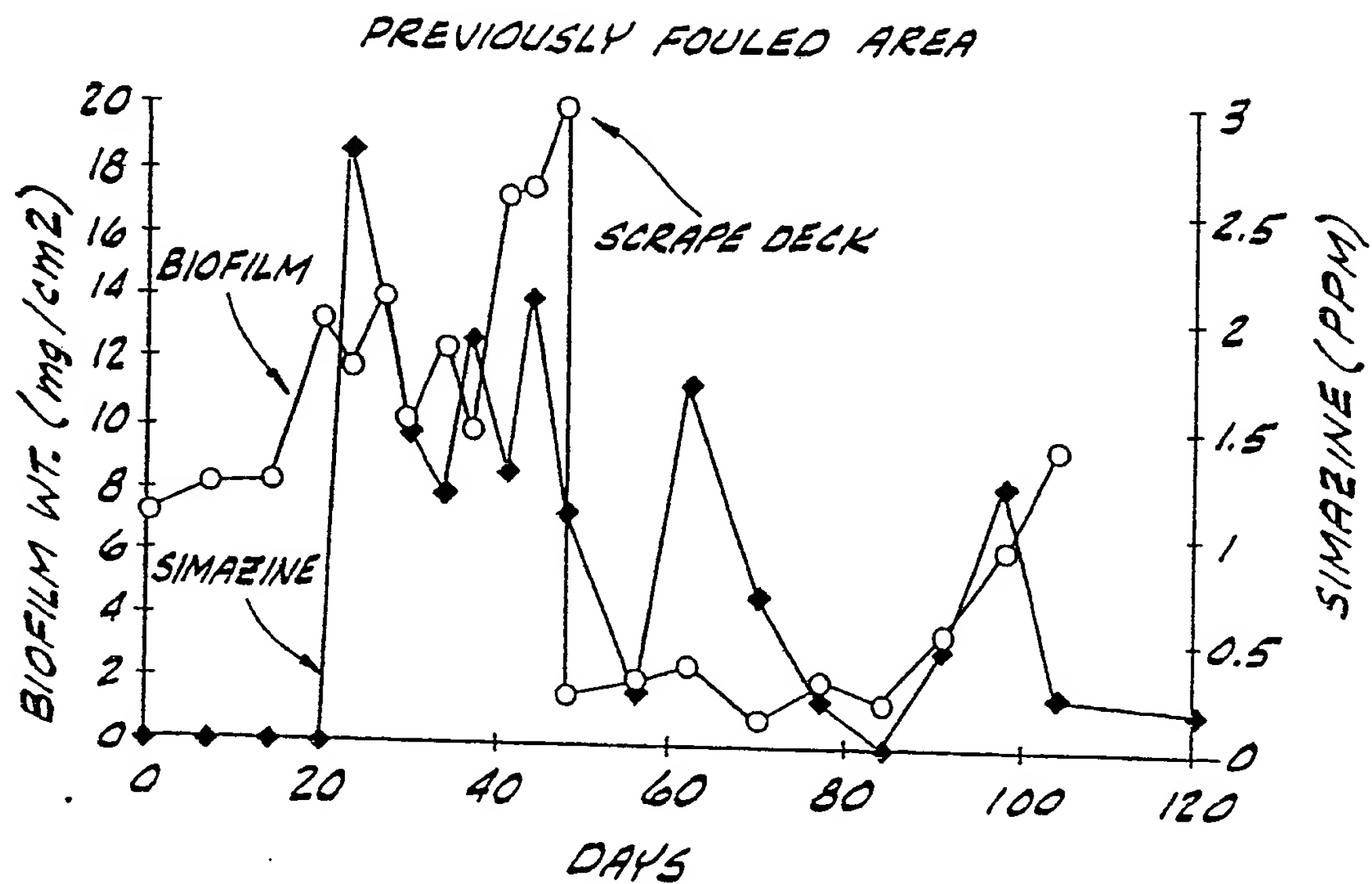
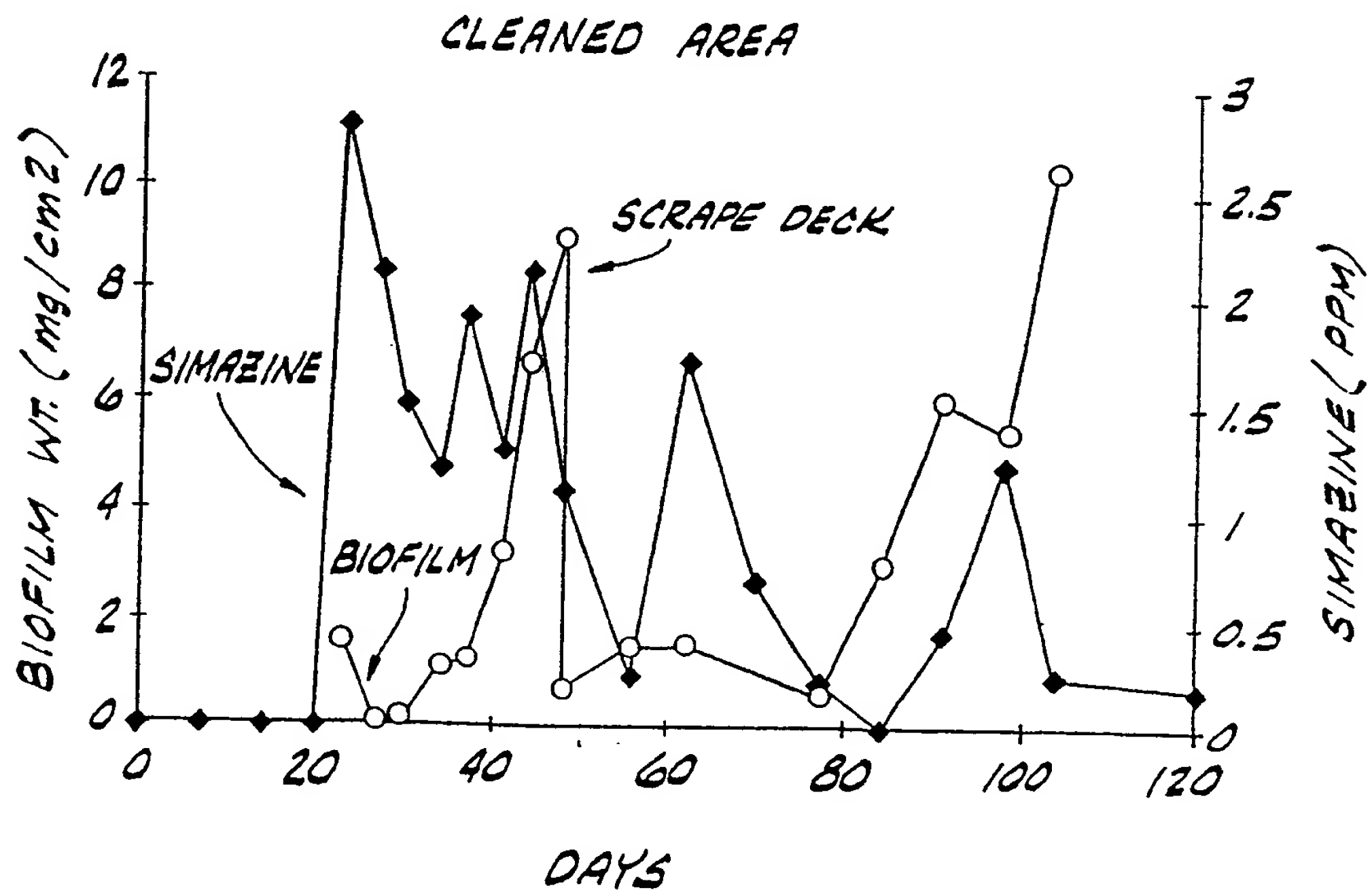



FIG. 3





# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/01700

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC(4): A01N 59/00 U.S.C1.: 71/67		
<b>II. FIELDS SEARCHED</b> Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
U.S.	71/67 514/245	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 4,659,359 (LORENZ) 21 April 1987, see entire document.	1-38
<p> <sup>10</sup> Special categories of cited documents:            "A" document defining the general state of the art which is not considered to be of particular relevance            "E" earlier document but published on or after the international filing date            "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)            "O" document referring to an oral disclosure, use, exhibition or other means            "P" document published prior to the international filing date but later than the priority date claimed            "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention            "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step            "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.            "&amp;" document member of the same patent family         </p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
18 JULY 1989		18 AUG 1989
International Searching Authority		Signature of Authorized Officer
ISA/US		 CATHERINE L. MILLS